Water Quality Review: Sierra Nevada 2007 Lake Monitoring

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Executive Summary

Twenty-five Wilderness lakes were sampled for acid-base water chemistry and water transparency between July and October 2007 as part of Project LAKES, the Sierra Nevada long-term lake monitoring project of the Pacific Southwest Region, USDA Forest Service Air Resources Program. After incrementally increasing the number of lakes sampled each year since 2000, 2007 was the first year that the complete network of lakes was sampled in all Class I Areas in the Sierra Nevada, southern Cascades, and northeastern California overseen by the Pacific Southwest Region of the USDA Forest Service.

Ten long-term monitoring lakes have records of between 6 and 22 years in length, long enough for preliminary statistical analysis for temporal change. None of these lakes experienced a significant decline in the primary indicator for acidification, acid neutralizing capacity (ANC). A statistically significant decline in sulfate, however, was identified for Waca and Smith Lakes, both in Desolation Wilderness immediately west of Lake Tahoe. At Waca the sulfate change is slight, from the 4-6 $\mu Eq\ L^{-1}$ range between 1985 and 1992 to the 2-3 $\mu Eq\ L^{-1}$ range since 2000. A similarly slight reduction in sulfate concentrations was identified at Smith Lake. These reductions parallel sulfate reductions identified elsewhere in the western US. Waca Lake also experienced minor decreases in calcium and chloride concentrations over time. A few other statistically significant temporal changes were identified for some of the ten lakes having six or more years of data. Because these changes were minor, and the duration of records at most lakes is still short, these changes do not appear to warrant further assessment at this time.

There is no current evidence suggesting either acidification or nutrient buildup in the lakes monitored in early summer 2007. Several lakes sampled in September and October 2007 also had no nutrient buildup or loss of acid buffering capacity.

A quality assurance review of the chemistry data identified a continuing "rebound" in the quality of the chemical analyses from 2004. For several metrics, the 2007 results are generally on a par with, or better than, the pre-2004 results. For instance, appreciably more of the samples were analyzed at a "higher quality" level for percent ion differences in 2007 than in any prior year other than 2002. Two exceptions to the improvement in quality assurance were (1) longer transit times for some samples—for the first time 18 days, and (2) sample labeling irregularities.

Ion imbalances evident in prior years persisted in 2006. This continuing imbalance suggests that one or more constituents causing the imbalance are not currently being analyzed. One candidate unanalyzed constituent, dissolved organic carbon (DOC), is being analyzed in 2007; a revised draft of this document presumably will include the DOC results when they become available.

Several lakes sampled in prior years located east of either the crest of the Sierra Nevada or the crest of the southern Cascades had higher nitrate and sulfate concentrations than lakes west of the crest. The 2007 results further support this west-east differentiation. In particular, Dana Lake, in Ansel Adams Wilderness near Yosemite Park had elevated sulfate and nitrate for the fourth consecutive year A variety of factors may be the cause of the high concentrations (Berg 2007), with geologic sources of sulfate a prime candidate and atmospheric deposition from sources in the alkaline Great Basin a nitrate source.

To begin to extend understanding of atmospheric effects on lakes in other sub-regions in California, two lakes in the North Coast Range, in Yolla Bolly-Middle Eel Wilderness (Mendocino/Six Rivers/Shasta-Trinity National Forests), were sampled. These lakes could be candidates for long-term monitoring. They had much higher concentrations of most chemical constituents than most lakes sampled in the Sierra Nevada.

Recommendations

1) Continue sampling at the "long-term" monitoring lakes.

The lake sampling is aimed at identifying human-caused changes in lakes in the Sierra Nevada. Because changes can be subtle several years are needed before supportable interpretations about trends in lake chemistry can be made. The network of long-term monitoring lakes is complete and project costs should drop because fewer lakes will be sampled than in prior years. Continued sampling is needed to determine if the chemistry of the Wilderness lakes is changing, and if so if atmospheric deposition is a cause of the changes. Each year the duration of monitoring for each lake grows so that continued monitoring will allow better estimates of trends in more lakes each year.

2) Emphasize sample labeling protocols in the annual refresher training.

Several 2007 samples had unorthodox and confusing labels that added appreciable time to the interpretation of the results. Emphasizing the need to follow the labeling protocols in the annual refresher training could reduce the likelihood of repeating the "mis-labeling".

3) Emphasize the need to double-check mailing labels in the refresher training.

Per Louise O'Deen (Rocky Mountain lab manger) the samples that took 18 days to reach the Ft. Collins laboratory apparently had illegible zip codes on the mailing labels. The likelihood of repeating this error could be reduced by re-iterating the need to double-check the correctness of the mailing information in the annual refresher training.

4) Follow-up the initial "short-core" diatom sampling with collection of a long core at Moat Lake in Hoover Wilderness.

The R5 Air Program partnered in 2007 with Professor James Sickman, University of California—Riverside, in the first phase of a diatom study at several Sierra Nevada lakes managed by the Forest Service. This study could provide essential scientific information for the establishment of critical loads for atmospheric deposition of acids and nitrogen in wilderness areas of the Sierra Nevada. This information would allow a more robust application of the PSD permitting process. To redeem the promise of this study, further coring, sediment dating, and model development is needed. A "long core" should be collected at Moat Lake to extend the time horizon for assessing conditions 100-200 years into the past.

5) **Continue the effort started in 2007 to develop a monitoring program for Yolla Bolly-Middle Eel Wilderness.**

Develop a plan for lake monitoring and depending on specifics of the plan, either sample more lakes as candidates for long-term monitoring, or select one or both of the Yolla Bolly lakes sampled in 2007 for inclusion in a long-term monitoring effort.

6) Continue sample collection in early summer (as currently done) and early autumn at readily-accessible lakes to help determine if the sampling regime could be simplified to an early autumn collection solely at lake outlets.

In many lake sampling projects outlet samples are collected in autumn when the lake is thermally mixed and an outlet sample adequately represents the chemistry of the entire lake. Outlet sampling would be faster and potentially less costly than mid-lake sampling. Although research conducted in the 1980s in the Sierra suggest that lake chemistry may differ appreciably between early summer and early autumn,

insufficient Forest Service data are currently available to determine if the chemistry of autumn outlet samples matches the chemistry of early-summer mid-lake samples. A decision to move to solely outlet sampling could be based on data from elsewhere, or from the 1980s Sierran research. Before making a decision on autumn outlet sampling a prudent approach is to concurrently collect both outlet and mid-lake samples at several long-term monitoring lakes at the end of snowmelt and again in early October, and compare the chemical concentrations. Several of these "seasonal" collections were conducted in 2006 and 2007 but additional collections could solidfy the preliminary results from 2006 and 2007.

7) **Assess the zooplankton data and decide whether to continue zooplankton sampling.**
Zooplankton samples were collected for several years at the long-term monitoring lakes. Although zooplankton taxonomy and metrics were reported for most of these data, no comprehensive analysis or interpretation of these data has been done. A comprehensive interpretation of the available zooplankton data would provide input on whether continued collection of zooplankton samples is worthwhile.

1.0 Introduction

Wilderness Areas are important national resources providing relatively unaltered natural landscapes for our enjoyment. Although watershed activities in Wildernesses are highly constrained, damage to some of these fragile resources is possible through short and long-range transport of air pollutants (Eilers 2003). For instance, Sickman et al. (2003) believe "…that lakes throughout the Sierra Nevada are experiencing measurable eutrophication in response to the atmospheric deposition of nutrients" and Fenn et al. (2003) document elevated nitrate levels in high-elevation Sierran lakes, reportedly from nitrogen deposition. To address this concern, in 2000 the Air Resources Program of the Pacific Southwest Region (Region 5) of the USDA Forest Service (FS) initiated lake monitoring in Class I Wilderness Areas of the Sierra Nevada, California Cascades and northeastern California. A monitoring goal of this program is to provide early indication of possible impacts associated with deposition of acid-rain precursors.

This report assesses and interprets water chemistry data collected in 2007 and compares these data against information obtained in prior years. This report does not directly specify the background context for lake or stream monitoring by the regional Air Resources Program. One objective of the monitoring, however, is to address the management goal of maintaining or improving aquatic, physical and biological air quality relate values (AQRVs) of "Class I" Wilderness Areas as mandated by amendments to the Clear Air Act and interpreted by the US Senate as an "affirmative responsibility by federal resource managers to err on the side of protecting AQRVs for future generations" (US Senate 1977).

2.0 Lake Monitoring Network

One intent of the Region 5 lake monitoring program is to follow the precedent of other FS regions by identifying a small number of lakes sensitive to atmospherically-driven acidification in each Class I Area and monitoring them over the long term. The premise is that monitoring lakes (operationally defined as water bodies greater than one hectare in area and greater than two meters in depth) particularly vulnerable to potential acidification will act as "a canary in a coal mine" and that their protection presupposes protection of less sensitive lakes.

Acid neutralizing capacity (ANC) is the single best indicator of lake sensitivity to acidification (Sullivan et al. 2001). Lakes with low ANC are sensitive to acidification, and low-ANC lakes provide information relevant to possible nutrient issues. The selection process for long-term monitoring lakes (those with low ANC) is not simple and requires a combination of modeling (Berg et al. 2005) and synoptic sampling prior to final selection. Twenty-three long-term monitoring lakes were sampled in 2007. These lakes were selected after a one-time synoptic sampling of many lakes in each Wilderness in which ANC and other chemical constituents were evaluated. 2007 is the first year that the complete network of lakes was sampled in a standardized manner. The network, including lakes in all Class I Wildernesses ranging from the Sierra National Forest in the southern Sierra Nevada (John Muir Wilderness) to the Modoc National Forest in the northeastern corner of California (South Warner Wilderness), is now complete and no other lakes are anticipated to be added (Figure 1) (Domeland Wilderness, the southern most Class I Area in the Sierra Nevada, has no lakes and is not included in the sampling network.

In addition to the 23 "long-term" lakes, two other lakes were sampled in Yolla Bolly-Middle Eel Wilderness, in north-coastal California, to provide a basis for longer-term monitoring. In 2007 25 lakes were sampled from twelve Wildernesses as follows:

Wilderness	Number of Lakes Sampled	Long-term Monitoring Lakes
Hoover	2	2
John Muir	6	6
Kaiser	1	1
Ansel Adams	3	3
Dinkey Lakes	1	1
Mokelumne	2	2
Desolation	2	2
Emigrant	3	3
Caribou	1	1
1000 Lakes	1	1
South Warner	1	1
Yolla Bolly	2	0

Four of the long-term monitoring lakes were sampled twice to continue to document any with-year temporal lake chemistry variation. Outlet as well as mid-lake samples were also collected at several of the long-term monitoring lakes, to provide information on the option to sample only outlets in the future.

One long-term monitoring lake, Waca in Desolation Wilderness, has been monitored twelve times since 1985; monitoring of the most of the other lakes began more recently:

Lake	Wilderness	Years of Data	Years Sampled
Powell	Emigrant	7	2000, 2002-07
Key	Emigrant	8	2000-07
Karls	Emigrant	5	2000, 2003-04, 2006-07
Long	Kaiser	7	2000, 2002-07
Patterson	S. Warner	6	2002-07
Mokelumne 14	Mokelumne	6	2002-07
Lower Cole Creek	Mokelumne	6	2002-07
Hufford	1000 Lakes	6	2002-07
Caribou 8	Caribou	6	2002-07
Waca	Desolation	12	1985, 1991-93, 2000-07
Smith	Desolation	8	1985-86, 1991-92, 2000, 2005-07
Walton	Ansel Adams	4	2004-07
Dana	Ansel Adams	4	2004-07
Little East Marie	Ansel Adams	4	2004-07
Walton	Ansel Adams	4	2004-07
Bullfrog	Dinkey Lakes	4	2004-07
East Chain	John Muir	2	2005, 2007
Treasure SE	John Muir	2	2005, 2007
Vermillion	John Muir	2	2005, 2007
Cottonwood 5	John Muir	2	2006-07
Bench	John Muir	2	2005, 2007
Cascade	Hoover	2	2006-07
Moat	Hoover	2	2006-07

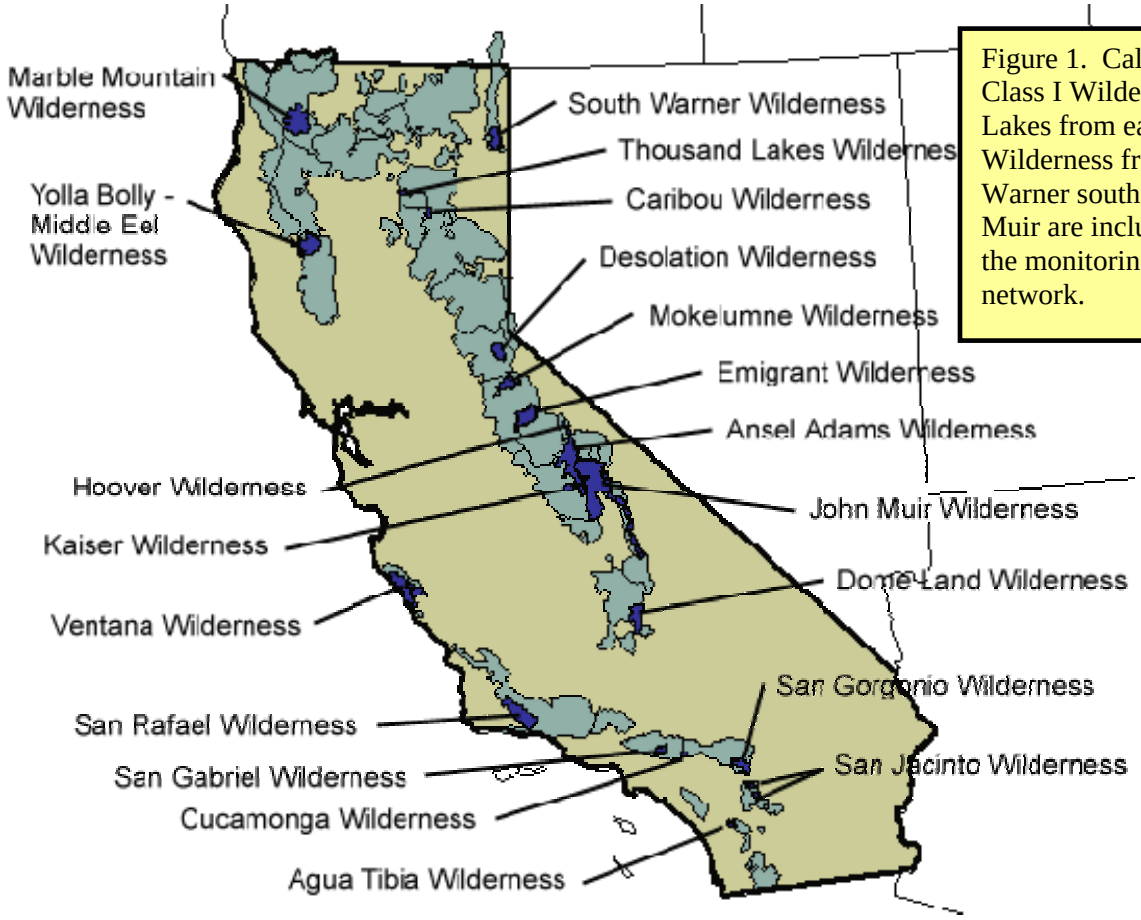


Figure 1. California Class I Wildernesses. Lakes from each Wilderness from S. Warner south to John Muir are included in the monitoring network.

This report addresses lake chemistry and transparency in the context of an early-warning monitoring program for acidification of Wilderness lakes. The monitoring program is not a research study, and relatively minor irregularities in the quality assurance results are not presumed to be causes for major concern.

3.0 Objectives

This report has four primary objectives:

1) Assess the quality of selected field procedures and laboratory analyses of lake water samples collected in 2007, specifically to identify any samples that may need re-analysis or that otherwise may require additional action (e.g., revision of sample type/label or deletion of the data).
2) Summarize the relationships between the 2007 lake chemistry data and information collected in prior monitoring (e.g., trends through time).
3) Address the option of modifying the sampling regime to collect only outlet samples in early autumn, rather than mid-lake samples in early summer.
4) Summarize related lake monitoring activities conducted in 2007 (e.g., diatom coring)

This report is not comprehensive in that some components of the 2007 (and earlier) data collection are not evaluated (e.g., data from field data sheets, including water temperature information, and zooplankton data). Nor are other potentially relevant components of the monitoring program comprehensively addressed (e.g., adequacy of training, dataset formalization).

4.0 Methods

To address the quality assurance objective, a variety of standardized techniques are available. This assessment focuses on commonly-used techniques described and exemplified in prior assessments for Forest Service lakes (e.g., Turk 2001, Eilers 2003, Eilers et al. 1998) and does not include all possible assessment procedures. The procedures evaluate (1) internal consistency of samples (e.g., transit time, ion balances, calculated versus measured ANC, calculated versus measured conductivity, and outlier assessment), (2) precision through analysis of duplicate samples, and (3) bias or contamination through assessment of field blanks. Lakes with unexpected chemical concentrations are identified in the outlier assessment. Each technique is described briefly below. The data were analyzed with either the Excel® or WQSTAT Plus® software packages.

All samples were analyzed at the USDA Forest Service Rocky Mountain Station analytical laboratory in Ft. Collins, Colorado (hereafter referred to as RM). Concentrations for the following constituents were assessed: conductivity, calcium, magnesium, sodium, potassium, ammonia, fluoride, chloride, nitrate, sulfate, phosphate and acid neutralizing capacity. Acidity, as pH, was also evaluated. Detection limits (mg/L and μEq L^{-1}) are listed below:

Sulfate	Sodium	Ammonia	Chloride	Potassium	Magnesium	Calcium	Nitrate
0.05/1.04	0.01/0.44	0.01/0.55	0.01/0.28	0.02/0.51	0.02/1.65	0.02/1.00	0.02/0.65

Several of the long-term monitoring lakes were sampled both near the surface (epilimnion), and at depth (hypolimnion) if they were thermally stratified; otherwise the thermally un-stratified long-term lakes were sampled approximately 1 m below the lake surface at a deep-water location. Samples from the two Yolla Bolly lakes were collected at their outlets, or if an outlet wasn't found, along the shoreline. To continue to assess potential differences between mid-lake and lake outlet chemistries, several long-term monitoring lakes were sampled at all three locations contemporaneously (outlet, epilimnion and hypolimnion) or both outlet and epilimnion concurrently. Specific sampling and monitoring protocols are detailed in Berg and Grant (2004) for the long-term lakes and in Berg and Grant (2002) for the lakes sampled at the outlet or along the shoreline.

Data analysis follows the draft protocol for long-term lake monitoring being adopted by the national Air Resources Program of the USDA Forest Service (Gurrieri 2006). The summarization objective addresses temporal change with time series plots and tests for statistical trends in chemistry for lakes with at least 6 years of data. The data are first checked for normality (Shapiro-Wilk procedure, Gilbert 1987), then trends are assessed by the nonparametric Mann-Kendall test, with statistically significant trends quantified by Sen's slope estimate (Sen 1968). Caution is needed in interpreting temporal trends for Waca and Smith Lakes because sampling over the years has been undertaken by different agencies and chemical analyses conducted at different laboratories. Differences in procedures could confound statistically significant temporal trends. Also the samples for trend analysis are from either mid-lake epilimnion or lake outflow locations. Although differences between these locations are typically understood to be minimal (Clow et al. 2002, Musselman 2004), they could also confound identification of temporal trends.

Recommendations for procedural changes, decisions needed and other actions are summarized at the beginning of this report and a listing of the 2007 chemistry data is given in Appendix I.

5.0 Results

5.1 Quality Assurance

5.1.1 Internal Consistency

5.1.1.1 Transit Time

After collection, samples need to be kept cool to preserve their chemical integrity. Sample warming elevates the risk of biological activity in the sample that could alter the concentration of some chemical constituents. Although refrigerant is included in sample mailing packages the refrigerant has an unknown, but probably relatively short, effective lifespan. All effort should be made to assure sample arrival at the analytical laboratory as soon as possible after collection. To this end a courier system is sometimes used to expedite shipping of samples from lake to trailhead. If needed, samples are stored in a refrigerator rather than mailed over a weekend.

The critical time period is not the total transit time, but the duration that a sample is kept cool by a short-lived refrigerant (e.g., "blue ice") versus a dedicated coolant (e.g., a refrigerator). Information is not readily available on the time duration samples were cooled by a short-lived refrigerant so the potential for sample degradation due to inadequate cooling can't be completely assessed. Nevertheless, in general the longer the time between sample collection and receipt at the lab, the greater the chance for sample degradation.

Ninty-three sample collections (including duplicates) were made from the 25 lakes sampled in 2007 (four lakes were sampled twice). Thirty-eight percent of the collections arrived at the laboratory within 3 days of sample collection (compared to 64% in 2003, 62% in 2004, 26% in 2005 and 38% in 2006). Almost 54% the collections in 2007 had transit times of 5 days or longer, with 9% of the samples in transit between 11 and 18 days. 2006 also had a relatively high percentage of transits taking 5 or more days, but no prior year had any transits longer than 12 days. Most of the 10+ day transits were from Mokelumne Wilderness. In prior years samples from this Wilderness had much shorter transit times. Chemical characteristics of the 11+ day transit samples are addressed in section 5.1.1.6 of this report. The mean transit time was over 5 days, up from 4 days in 2006.

For the first time in the history of the LAKES project many samples from the same lakes (collected on the same dates) had differing transit times. In the extreme, single samples from Lower Cole Ck and Moke14 lakes took a week longer in transit time than the other samples from these lakes collected on the same dates. Although the reason(s) for the varying transit times aren't completely known, per Louise O'Deen (RM lab manager) some FedEx shipments definitely took longer than anticipated. O'Deen further stated that apparently some of the zip codes on the FedEx mailing labels were illegible.

The long sample transit times are not a good sign and the trend toward longer transit times in 2006 and 2007 suggest a need for more scrutiny by project staff on reasons for the extended transit times. Among other things, more attention to clarity on the shipping labels may be warranted.

Transit time (days)	**Number of Lakes**					
	2007	**2006**	**2005**	**2004**	**2003**	**2002**
1	0	1	1	0	0	1
2	7	6	8	14	3	6
3	9	6	2	4	4	3
4	4	3	7	0	2	25
5	6	6	4	4	1	5
6	4	2	15	5	0	1
7	8	6	4	1	1	1
8	4	0	1	1	0	0
>8	5	4	0	0	0	0

5.1.1.2 Ion Balance

A basic premise in ion balance determinations is that the sum of the negatively charged constituents (anions) should balance the sum of the positively charged constituents (cations) in each sample. Analytical procedures are not perfect so typically the ion balance is not exact for a set of samples. Ideally, however, there should be no bias; the sum of the cation minus anion concentrations for a set of samples should approximate zero. Bias is often attributed either to laboratory error or lack of testing for one or more cations or anions. Several related techniques address ion balance, either for potential problems with specific samples or as indicators of overall trends among samples.

Considered as a whole, the chemistry of the 2007 lake samples is slightly biased (Figure 2), and has a consistent under-estimation of the anions or over-estimation of the cations. Over 88% of the 2007 non-blank samples have a greater cation sum than anion sum, and there is an overall average of 7.5 $\mu Eq\ L^{-1}$ cation excess/anion deficiency per sample. This bias compares with averages in 2007, 2006, 2005, 2004, 2003, 2001 and 2000 of 13.3 13.3, 16.4, 15.9, 9.1, 10.7 and 8.75 $\mu Eq\ L^{-1}$ respectively. Although continuing cation excess/anion deficiency bias has been evident during every year of sample analysis, by the average deficiency metric the 2007 bias is less than in prior years.

A four-quadrant plot (Figure 3) provides additional information on the cation excess-anion deficiency issue. This plot shows that the bias is best characterized as equally an under-estimation of anions or an over-estimation of cations. This characterization differs from a consistent anion under-estimation through all prior years of the project. The more balanced bias in 2007 is a positive sign implying less overall bias.

The three samples not plotted in Figure 3 are from two lakes that are atypical of the chemistry of the rest of the 2007 dataset. The three samples are from Yolla Bolly Wilderness, not the Sierra Nevada/South Cascades location comprising the remainder of the sampling locations. The Yolla Bolly samples have concentrations often an order of magnitude higher than the Sierra/Cascades samples. Relatively small percentage differences in these high concentration samples can be large absolute differences, and the large absolute differences are reflected in the figure.

The ion imbalance has been evident during all years of sample collection. Samples from dilute waters in other areas can have a similar imbalance, and the relatively improved bias in 2007 (versus earlier years) suggests that the ion balance in 2007 is not a major problem.

5.1.1.3. Cation and Anion Sums

The ion balance calculations in section 5.1.1.2 address the chemistry datasest as a whole. For individual samples Turk (2001) identified two triggering values for cation/anion sum problems—to meet "mandatory" and "higher-quality" levels of data quality:

Total Ion Strength (cations + anions) ($\mu Eq\ L^{-1}$)	**% Ion Difference—Mandatory**	**% Ion Difference—Higher Quality**
<50	>60	>25
50-100	>30	>15
≥100	>15	>10

Both sets of criteria are percent-based and take into account the fact that percentage values increase for the same absolute differences in concentrations as concentration levels decrease. The percent of samples meeting the two criteria are listed below for monitoring years 2002-2007:

Year	% Meeting Mandatory Criterion	% Meeting Higher Quality Criterion
2007	99	85
2006	99	74
2005	91	73
2004	90	20
2003	100	83
2002	100	87

In comparison to earlier years, the 2007 data are of high quality in that a higher percentage of the samples in 2007 than in most other years meet the higher quality criterion.

The one 2007 sample not meeting the mandatory criteria is from the shoreline of Long Lk (Kaiser Wilderness), and many of the samples not meeting the higher quality standard are from Long and Powell (Emigrant Wilderness) Lakes.

5.1.1.4 Calculated versus Measured ANC

Another index of potential ion imbalance is the comparison of measured ANC against ANC calculated as the difference in the sum of base cations (calcium + magnesium + sodium + potassium) and acid anions (sulfate + chloride + nitrate). A bias similar to the historical/pre-2007 ion imbalance also exists for the 2007 ANC comparison (Figure 4). The calculated value on average is 7.5 $\mu Eq\ L^{-1}$ greater than the measured value (compared to 11.6 $\mu Eq\ L^{-1}$ greater in 2006, 15.8 $\mu Eq\ L^{-1}$ greater in 2005, 15.65 $\mu Eq\ L^{-1}$ greater in 2004 and 7.55 $\mu Eq\ L^{-1}$ greater in 2003), with 90% of the individual samples having greater calculated than measured ANC. The 7.5 $\mu Eq\ L^{-1}$ average is conditioned largely by two high-ANC samples from lakes in Yolla Bolly Wilderness. Without these two samples the average calculated ANC drops to 6.5 $\mu Eq\ L^{-1}$ greater than the measured value. Thirty-one percent of the non-blank 2007 samples had calculated minus measured ANCs > 10 $\mu Eq\ L^{-1}$ (compared to 43% in 2006, 54% in 2005, 80% in 2004 and 27% in 2003). Eilers et al. (1998) label samples having calculated minus measured ANCs > 5 $\mu Eq\ L^{-1}$ as "outliers". By this definition over 59% of the 2007 samples would be "outliers" (compared to 42% in 2006, 79% in 2005 and over 92% in 2004). Although the imbalance between calculated and measured ANC is further evidence that either one or more constituents aren't being analyzed--or there are laboratory problems--by this measure the 2007 sample analysis is of higher quality than analyses from most of the prior years.

The absolute value of the difference between measured and calculated ANC is greater than 20 $\mu Eq\ L^{-1}$ only for the Long Lk samples. This compares to five lakes sampled in 2006 with greater than 30 $\mu Eq\ L^{-1}$ absolute value of the difference between measured and calculated ANC. The quality of the 2007 analyses may therefore be improved over 2006, or the 2006 lakes may have had properties causing greater variability than the 2007 lakes.

5.1.1.5 Theoretical versus Measured Conductivity

The measured versus theoretical conductivities from the 2006 lake samples show most samples (96%) to be within the +/-1 $\mu S\ cm^{-1}$ criteria used by Eilers et al. (1998) to identify "outlier" values (Figure 5). The 96% value is better than prior years (86 in 2005 and 2006, and 88 in three prior years. Four samples collected in 2007 exceeded Eilers et al.'s +/- 1 $\mu S\ cm^{-1}$ criteria. Three of these were from the two lakes in the Yolla Bolly Wilderness having conductivities and ANCs much higher than the Sierran lakes. With high conductivities to begin with, it's not surprising that the difference between measured and theoretical conductivity is relatively large. In 2006 seven samples exceeded Eilers et al.'s +/- 1 $\mu S\ cm^{-1}$ criteria.

Per this metric there is little bias in the 2007 samples—50% of the non-blank samples have greater measured than calculated conductivity (compared to over 70% in 2006, 89% in 2005, 80% in 2004 and 75% in 2003)—and the mean bias is small, 0.13 $\mu S\ cm^{-1}$. Eilers (2003) described Gallatin National Forest lake samples with double this bias as not presenting "… a significant concern with respect to the quality of the data".

5.1.1.6 Outliers

Outliers are extreme values that are inexplicable. Contamination by body contact with sample liquid, for instance, is typically identified by outlier values of sodium and chloride. For all 2007 non-blank samples, concentrations of calcium, sodium, magnesium, ANC, chloride, nitrate and sulfate are plotted in Figure 6. Outliers are assessed visually and statistically using Dixon's outlier test. None of the samples with the unexpectedly long (e.g., 18 day) transit times were identified as outliers in either the visual or statistical assessments. These samples are therefore retained within the dataset.

5.1.1.6.1 Visual assessment

Four samples, two from each of two lakes, Long and Square in Yolla Bolly Wilderness, had particularly high concentrations of calcium, sulfate and ANC (Figures 6a and b). Because the duplicate samples from Square and Long Lakes have approximately equal concentrations for those constituents, the high concentrations from these lakes do not appear to be due to either a sample collection or laboratory error. Other lakes with moderately high 2007 concentrations of some constituents (e.g., Dana—nitrate =10 $\mu Eq\ L^{-1}$, sulfate = 74 $\mu Eq\ L^{-1}$, calcium = 83$\mu Eq\ L^{-1}$, Patterson—ANC = 160 $\mu Eq\ L^{-1}$, calcium = 70 $\mu Eq\ L^{-1}$, Bench—nitrate =10 $\mu Eq\ L^{-1}$, calcium = 84 $\mu Eq\ L^{-1}$) also had similar concentrations in prior years, and consequently aren't considered to be outliers. In particular Dana Lake, in Ansel Adams Wilderness a few kilometers east of Yosemite National Park near Tioga Pass, had high sulfate and nitrate concentrations when sampled in 2004, 2005 and moderately high sulfate in 2006. The high concentrations at Dana for four years running suggest that the concentrations there are real and not due to a procedural problem. Also, some lakes sampled in the 1985 Western Lake Survey (Landers et al. 1987) had high calcium and sulfate concentrations (e.g., Hoover Lake in Hoover Wilderness, with sulfate = 386 $\mu Eq\ L^{-1}$ and calcium = 493 $\mu Eq\ L^{-1}$). And lakes outside of the Sierra commonly have higher concentrations. For instance, the mean calcium and ANC concentrations of 1,798 lakes surveyed in the Eastern Lake Survey were 245 and 264 $\mu Eq\ L^{-1}$ respectively (Kanciruk et al. 1986).

5.1.1.6.2 Statistical assessment

Dixon's outlier test (Dixon 1953, NIC 2005) assumes data are distributed normally or log normally and tests whether a suspect value fits the distribution of the rest of the data set. At the 0.05 level of statistical significance, Dixon's test identified no outliers for ANC, calcium, chloride, potassium, magnesium, sodium, nitrate or sulfate at any lake. Conductivity and pH outliers were identified for Square Lake in Yolla Bolly Wilderness. Both lakes in Yolla Bolly have chemistries that appear to differ appreciably from the lakes monitored in the Sierra Nevada, southern Cascades and northeastern California. Concentrations of nearly all chemicals at Square and Long Lakes are much higher than at the other lakes. For this reason the conductivity and pH outliers at Square aren't considered to be true outliers but rather identified as outliers by Dixon's test simply because they are indeed much different than the concentrations at the other lakes.

Ammonium outliers were identified from single samples taken from Wahoo and Karls Lakes (John Muir and Emigrant Wildernesses respectively). At Wahoo the concentration was 1.66 $\mu Eq\ L^{-1}$ and at Karls the concentration was 1.50 $\mu Eq\ L^{-1}$. Ammonium concentrations in 2007 were generally lower across all lakes than in prior years. Also, ammonium, along with nitrate, are distinctive constituents in that their concentrations have always often been near, at or below the laboratory detection limit for the dilute

Wilderness lake samples. For instance, of 93 samples analyzed in 2007 for ammonium, 78 were below the detection limit. This high percentage of below-detection samples can cause even relatively moderate concentrations of above-detection samples to be identified statistically as outliers. Further, in prior years both of these lakes had ammonium concentrations equal to or greater than the 2007 concentrations (in 2006 ammonium in the two Karls Lake samples was 2.1 and 2.3 μEq L^{-1}, and in 2005 the single Wahoo Lake sample was 1.5 μEq L^{-1}). For these reasons it does not appear that the ammonium concentrations from Wahoo and Karls Lakes in 2007 are problematic, and the concentrations are retained in the dataset.

5.1.2 Precision -- Duplicate Samples

Forty-five "duplicate" pairs of samples were collected in 2007 from shallow mid-lake locations (22 lakes), at lake outlets or along the shoreline (16 lakes), and seven samples from the hypolimnion. All of the epilimnion and shoreline/outlet duplicates were collected about 5 minutes apart; the time period between collection of the hypolimnion duplicates was slightly longer. These duplicates should be nearly identical in their constituent concentrations. A measure of chemical variation, the percent relative standard deviation (%RSD), was calculated for all duplicates for ANC, calcium, nitrate, conductivity, magnesium, sodium, chloride, potassium and sulfate concentrations. Per B. Gauthier (5/30/02 email to J. Peterson) the %RSD for duplicate samples should be less than or equal to 10%. For each constituent the following table lists the percentage of the pairs of duplicate samples with %RSD greater than 10% for samples collected between 2001 and 2007:

	2007	2006	2005	2004	2003	2002	2001
Number of Duplicate Pairs	45	18	9	8	14	11	12
Chemical Constituent							
ANC	33	33	44	43	23	55	8
Calcium	22	0	11	14	38	36	25
Nitrate	79	61	0	29	8	0	9
Conductivity	0	0	22	0	46	18	17
Magnesium	44	0	11	29	8	36	8
Sodium	7	0	22	14	8	9	8
Potassium	38	22	22	57	8	18	8
Chloride	47	28	56	29	23	27	17
Sulfate	18	17	22	0	23	9	25

For the %RSD metric—

- Compared to earlier years the 2007 duplicate samples were less precise than 2006 and for nitrate and magnesium had the highest %RSD (lowest precision) of any year on record.
- Most constituents have relatively high values for most years, implying a fair amount of "noise" in the laboratory analyses, the sample collection, handling and transport procedures, or both.

The %RSD calculation procedure is sensitive to "sample size". Calculation of standard deviations on the basis of two values is marginal; typically at least three values are used, and ideally a much larger sample size should be the basis for the %RSD calculation. The relatively high values listed in the table above for some years may be partially due to this sample size effect.

Another reason for some relatively high %RSD values, particularly for nitrate, may be low concentrations, near or below the detection limit. For instance, the concentrations of the two nitrate duplicates from outlet samples taken from Caribou#8 in 2007 were very low, 0.016 and 0.113 μEq L^{-1}. Nevertheless the %RSD for these duplicates is 106%, much greater than the 10% threshold value. Also

the 2007 median difference in nitrate, sulfate, ammonium, and magnesium is below 0.05 μEq L^{-1}, a very low magnitude. This low median difference suggests that although the 2007 %RSD values for some duplicate are high, the absolute value of the differences is generally small. Last, for nitrate and ammonium in particular, many samples have had undetectable concentrations during most years, suggesting that these constituents occur in very low concentrations in the lakes sampled.

ANC is the single best constituent for %RSD assessment because it tends to integrate the concentrations of several of the other constituents. ANC is also the single best correlate with potential acidification. The highest %RSD value (40) from the 2007 epilimnion sample collections was from Bullfrog Lk, the only lake sampled in Dinkey Lakes Wilderness. The 40 %RSD value was almost twice that of the second greatest ANC %RSD from 2007. Although the Bullfrog ANC values were relatively low, 14.3 and 25.8 μEq L^{-1}, the difference in the two values is appreciable. The 2007 14.3 and 25.8 μEq L^{-1}values compare to 23, 24 and 22 μEq $L^{-1}$from epilimnion or outlet samples collected in earlier years. This comparison suggests that the 2007 14.3 value may be low. On balance, however, there's no clear reason to delete the 14.3 value and it is retained in the database.

Most of the 2007 duplicates had only one or two %RSD values greater than 10. One duplicate pair, from Little East Marie Lk (Ansel Adams Wilderness), however, had %RSD values greater than 40 for sulfate, magnesium and hydrogen. In 2004, the only other year with duplicate sample collections at Little East Marie Lk, the %RSD values were generally low There's no obvious reason why the 2007 samples had higher %RSD values than most others, nor does there appear to be any need for closer scrutiny of either laboratory or field procedures. I interpret the relatively high %RSD values for Little East Marie Lk to be largely the result of random errors.

The mean absolute differences between the duplicates (the precision) for major chemical constituents are compared below for years 2003 through 2007:

Constituent	**Unit**	**Mean Absolute Difference**				
		2007	2006	2005	2004	2003
ANC	μEq L^{-1}	3.36	4.33	3.62	2.35	3.18
Conductivity	μS cm^{-1}	0.34	0.30	1.36	0.49	0.22
Calcium	μEq L^{-1}	2.48	0.85	1.08	1.34	1.91
Magnesium	μEq L^{-1}	0.84	0.30	0.29	0.80	0.72
Sodium	μEq L^{-1}	0.65	0.29	1.12	2.70	0.72
Potassium	μEq L^{-1}	0.50	0.26	8.81	1.91	0.34
Chloride	μEq L^{-1}	0.53	0.17	7.94	0.16	0.62
Sulfate	μEq L^{-1}	1.22	0.89	0.20	0.33	0.24
Nitrate	μEq L^{-1}	0.20	0.20	0.03	0.25	0.09

Compared to the earlier years, the 2007 results are about average for all constituents except calcium, magnesium, and particularly sulfate, for which the 2007 differences are greater.

In a study of lake waters on the Mt. Baker-Snoqualmie National Forest in Washington, Eilers et al. (1998) characterized samples with mean absolute differences $\leq$ 1.0 μEq L^{-1} as dilute waters. Except for ANC, calcium and sulfate, the 2007 Sierran samples match this criterion for dilute lake water.

5.1.3 Bias -- Field Blanks

To help assure that water collection bottles are not contaminating samples, "field blanks" have water—typically de-ionized with very low or undetectable constituent concentrations—that is stored in the bottles for time periods comparable to the amount of time sample water remains in a bottle prior to analysis. Field blanks are typically sent out by the laboratory with the other bottles and taken to the field along with

the actual sample bottles. Common contaminants in the field blanks are sodium and chloride, from perspiration, or elevated acidity as a residue from prior cleaning of the bottle. The QA/QC protocol for the chemistry laboratory at the Riverside unit of the Forest Service's Pacific Southwest Research Station states that "[T]he value of a blank reading should be less than $\pm$0.05 mg L^{-1} from zero". Eilers et al. (1998) used 1.0 μEq L^{-1} for individual catons as a trigger value for blank contamination and the FS national air program (USDA Forest Service 2007) states that ideally conductivity in blanks should be less than 2 uS/cm.

Six field blanks were incorporated into the 2007 sample collection. Fifty percent of 60 constituent analyses (ten constituents for each blank) had detectable results, compared with 42% in 2006 and 33% in 2005. Contrary to prior years, when many of the blanks had detectable calcium concentrations, in 2007 more blanks had detectable chloride, phosphate, and sulfate than calcium. None of the 30 detections were $\geq$ 0.05 mg L^{-1}, PSW Riverside's threshold value. Seventeen percent of the detections were $\geq$ 1.0 μEq L^{-1}, Eilers et al.'s (1998) criterion for individual ions (down from 30% in 2006) and conductivity in all six blanks ranged from 1.23 to 1.85 uS/cm. The highest concentration was 2.1 μEq L^{-1}, for calcium, as in 2006. None of the detected concentrations were particularly high and the detections appear to be randomly distributed among the nine field blanks (in other words, no single sample/lake or samples had a preponderance of detections).

In summary, the field blank assessment does not appear to identify a systematic problem with sample collection. Nor does it identify any individual problematic samples or individual constituents.

5.1.4 Summary of Quality Control Findings

The 2007 quality control analyses did not identify any new or unexpected issues, and for several QA/QC metrics the 2007 data are better than in several prior years. There were no true outliers or salt-contaminated samples as in some earlier years. Although the transit time for water samples from collection to arrival at the chemistry lab was longer in 2007 than any other year, ion imbalance, ion sum, calculated vs. measured ANC and theoretical vs. measured conductivity metrics were better than in many prior years.

5.2 Time Trends for Long-term Monitoring Lakes

Ten lakes have been monitored at least six times (see table on page 5), with one of these, Waca in Desolation Wilderness, sampled twelve times since 1985. A monitoring duration of 5 or 6 years is minimal for preliminary assessment of temporal change, and the literature suggests that typically a much longer time period is needed before temporal trends can be statistically verified. To offer a preliminary assessment of temporal change, plots of the chemistry of the five lakes are presented in Figure 7, and the results of a trend analysis are presented.

The magnitudes of concentration changes between years are typically small, usually much less than one μEq L^{-1} annually. During development of the monitoring component of the Sierra Nevada Framework extensive research identified that annual ANC, sulfate and nitrate changes less than 30% would not be cause for alarm (personal communications, Al Leydecker and Jim Sickman 2000). The percent changes in Figure 7 are typically less than 30%, even for the very low concentrations levels at which very low absolute differences would generate relatively large percentage differences.

The following table summarizes the results of the temporal trend analyses. Normality testing, for each constituent at each location, showed that about 20% of the constituents were not normally distributed. To standardize the trend analyses and to be conservative, non-parametric trend testing was undertaken for all constituents. Hyphenated cells signify a non-significant trend (at $\alpha = 0.10$). Numerical values are the Sen slope estimate (Sen 1968) of significant temporal trends based on the Mann-Kendall test (Gilbert

1987). A negative value signifies a significant downward trend so that, for instance, over the sampling period sulfate at Waca Lake decreased approximately 0.14 μEq L^{-1} per year.

Lake	Constituent									
	ANC	Ca	NO3	SO4	Cl	K	Mg	Na	NH4	pH
Waca	--	-0.17	--	-0.14	-0.07	--	--	--	--	--
Long	--	--	--	--	--	--	--	--	--	--
Powell	--	--	--	--	--	--	--	--	--	--
Key	--	--	--	--	--	--	--	--	--	0.03
Smith	--	--	--	-0.11	--	0.03	--	--	--	--
Patterson	--	--	--	--	--	--	--	--	--	0.07
Mokelumne14	--	--	--	--	--	--	--	--	--	--
Lower Cole Ck	--	--	--	--	--	--	--	--	--	--
Hufford	--	--	--	--	--	--	--	--	--	--
Caribou8	--	--	--	--	--	--	--	-0.27	--	--

5.2.1 Waca

Waca Lake is located immediately west of the crest of the Sierra Nevada at approximately 2495 m elevation about 12 km southwest of Lake Tahoe. It is one of many adjacent lakes in the Desolation Valley section of Desolation Wilderness. Waca is a headwater lake in granodiorite terrain with very little vegetation on its watershed. The lake occupies about 2 hectares within a 10-hectare, south-west facing watershed. During surveys between 2002 and 2004 the maximum water depth at Waca was about 11 m, and a Secchi disk was visible at the lake bottom.

Waca Lake has the longest monitoring record in the Region 5 network, now twelve samplings, starting with the Western Lake Survey in 1985 (Figures 7a and 7b). A down trend in sulfate, first identified at Waca in 2004, parallels the general trend downward in the atmospheric wet deposition and sulfate concentration recorded at long-term deposition monitoring locations in Yosemite and Sequoia-Kings Canyon National Parks (NADP 2006). At Waca sulfate concentrations in the 4-6+ μEq L^{-1} range between 1985 and 1993 have more recently dropped to the 2-3+ range, with the lowest recorded value, 1.7 μEq L^{-1} in 2006.

Calcium and chloride have also decreased over time at a statistically significant rate. The changes for these constituents are small and for calcium may be influenced by one very low value (0.6 μEq L^{-1}) in 2004. 2007 is the first year a statistically significant chloride change was identified and 2007 is the second year with a statistically significant calcium change. The low rates of change do not suggest that any management action need to be taken.

Neither Waca Lake, nor any of the other Sierran lakes assessed here, show a significant temporal trend (at $\alpha = 0.10$) for nitrate or ANC, two important indicators of potential acidification or undesirable nitrogen fertilization. Theoretically, increases in sulfate and nitrate, and a decrease in ANC over time, could be a precursor to acidification, although alternative explanations for changing levels of these constituents are possible.

The 30% change criterion, mentioned above as an indicator of potential concern, is met for sulfate and marginally for ANC. These higher percent changes are not believed to foretell acidification because (1) sulfate is decreasing over time, rather than increasing as would be expected as a precursor for acidification, and (2) a single low ANC concentration, from 2001, causes the 30% criterion to be triggered. The low concentration is followed in 2002 through 2007 with ANC levels similar to prior years. ANC concentrations in the 1-2 μEq L^{-1} range (as in 2001) are at the edge of the resolution band for typical laboratory analysis; values in this range are less reproducible than higher values.

5.2.2 Key

Key Lake, located in the north-central portion of Emigrant Wilderness at 2799 m elevation and almost due east of San Francisco, drains a west-facing catchment approximately 6 hectares in area. This headwater lake is small, at 1 hectare area. The bedrock geology is similar to much of the Sierra Nevada dominated by felsic materials such as granodiorite, diorite, tonalite and felsic gneiss and schist. There is very little vegetation in the Key Lake watershed. Key Lake is relatively shallow, about 3 m maximum depth, and during surveys between 2002 and 2004 a Secchi disk was visible at the lake bottom.

ANC dropped at Key Lake from the 8-10 $\mu Eq\ L^{-1}$ range between 2000 and 2003 to less than 1.4 $\mu Eq\ L^{-1}$ in 2004 and 2005, causing a significant change in ANC at Key Lake for the six survey years from 2000 to 2005, but the 2006 and 2007 values "rebounded" to at or near the recorded maximum (Figure 7c). There were no statistically significant changes in 2007 for ANC, sulfate or nitrate at Key Lake. Data from future years are needed before interpreting further the ANC changes.

Some of the year-to-year ANC, sulfate and nitrate differences meet the 30% triggering value. However, except for ANC, the absolute value of the yearly differences are small, typically less than 2 $\mu Eq\ L^{-1}$, and probably not practically significant.

None of the constituent concentrations plotted in Figure 7d show an obvious trend through time; increases are typically followed by decreases (or vice versa), and none of the trends are statistically significant. Because pH is scaled logarithmically a 10-fold change in hydrogen ion concentration is represented by a one unit change in pH. Consequently plotting of pH on a linear scale masks changes. At Key Lake a statistically significant increase in pH was identified for the first time in 2007 (from the 5.6-5.8 range in 2000 and 2001 to the 5.86 to 5.95 range between 2005 and 2007. The change is small, 0.03 pH unit, and not believed to be practically significant.

5.2.3 Long

Long Lake occupies a moderately large (63 ha), north-facing headwater catchment in the northeastern section of Kaiser Wilderness about 75 km northeast of Fresno. At 2725 m elevation, Long Lake is in the same general elevation range as most of the other lakes assessed for temporal trends. It has more vegetation than many other Sierran wilderness lakes, with about one-half of the granodiorite-dominated catchment in vegetation identifiable from aerial photos. The lake occupies about 3.8 ha area and is backed by a 400-m headwall immediately due south. During surveys between 2002 and 2004 a Secchi disk was visible about one-half the way to the maximum depth of the lake (15 m).

ANC at Long Lake is higher than at most of the other lakes addressed in this section, and was in the high 20 to high 30 $\mu Eq\ L^{-1}$ range between 2000 and 2007 (Figure 7e). Calcium and sodium concentrations are also slightly higher at Long than the other Sierran lakes. No trends through time are identified for this lake, and any incipient increases through time—for instance for sodium and potassium between 2000 and 2004—were negated by downturns in later years (Figure 7f). Except for ANC, calcium and sodium, year-to-year changes for the other constituents have typically been 1 to 2 $\mu Eq\ L^{-1}$ and none of the annual ANC, sulfate or nitrate concentration changes meet the 30% criterion.

5.2.4 Powell

Powell Lake drains a north-facing, 32-ha catchment in the western portion of Emigrant Wilderness. This headwater lake is slightly lower down on the western slope of the Sierra than most other long-term monitoring lakes in the LAKES network. Powell's area is about 1.6 ha and its elevation is 2685 m. As with many of the other lakes detailed here, Powell's catchment is dominated by granodiorite. Almost

one-half of the catchment is well-vegetated. Between 2002 and 2004 Secchi disk transparency ranged from 4.5 to 6.75 m and maximum lake depth was about 8 m.

No statistically significant trends through time were identified for any chemical constituent. Similar to Long Lake, at Powell there has been very little variation through time in conductivity, magnesium, potassium, ammonium and sulfate (Figures 7g and h). Similar to most Sierran lakes nitrate concentrations have been very low, and at Powell were below the detection limit for all five surveys between 2000 and 2005. None of the annual ANC, sulfate or nitrate concentration changes at Powell Lake meet the 30% criterion and if anything ANC may be increasing over time.

5.2.5 Smith

Smith Lake, located about 4 km west of Waca Lake at the western edge of Desolation Wilderness, lies in a west-facing catchment with a 300-m headwall immediately east of the lake. This 2649 m elevation lake occupies about 10% of its 35-ha granite-dominated catchment. Mapping software identifies Smith Lake as dammed. A concern is that chemicals could leach from a dam and confound assessment of atmospheric effects on the lake's chemistry. Field work identifies the dam as a small wooden one that presumably is not influencing lake water chemistry in terms of atmospherically-derived chemical constituents.

Besides Waca Lake, Smith Lake is the only long-term lake with a statistically significant temporal trend for sulfate. As with Waca, the trend is relatively small, 0.11 $\mu Eq\ L^{-1}\ yr^{-1}$. Sulfate concentrations dropped from the 6-8 $\mu Eq\ L^{-1}$ range in the mid-1980s to the 4-5 $\mu Eq\ L^{-1}$ range more recently. A minor (0.03 $\mu Eq\ L^{-1}\ yr^{-1}$) increase in potassium was identified for the first time in 2007 and to varying degrees, other constituents share visually decreasing and increasing ionic concentration patterns through time (Figures 7i and j). The patterns may be due partly to potentially differing sampling protocols and (or) laboratories analyzing the samples. For instance at Smith Lake in 1985 and 1986 the samples were analyzed by K. McCleneghan, a contract researcher for the California Air Resources Board (McCleneghan et al. 1987), in the early 1990s by the University of California, Santa Barbara, and since then by RM.

The ANC drop from 15.5 $\mu Eq\ L^{-1}$ in 2006 to 9.4 $\mu Eq\ L^{-1}$ in 2007 meets the 30% criteria for concern (Figure 7i) suggesting ANC at Smith Lake should be closely monitored in the future.

5.2.6 Patterson

Patterson Lake, located about 29 km east southeast of Alturas, is the largest (8.6 ha) and deepest (35 m) lake monitored. At 2750 m elevation, Patterson Lake sits on volcanic terrain in a 35 ha, northeast-facing catchment 200 m below Warren Pk, on the crest of the Warner Mountains. As one of the few lakes in the S. Warner Wilderness, Patterson experiences relatively high recreational use. Paleopollen and charcoal information may be available for this lake as part of a PhD dissertation by Thomas A. Minckly. Patterson appears to be less transparent than most of the Sierran lakes surveyed, with a Secchi disk visible only to 2 m depth between 2002 and 2004.

Probably because it sits on volcanic terrain—and potential atmospheric inputs from the Great Basin to the east--the chemistry of Patterson Lake differs appreciably from lakes being monitored in the Sierra Nevada (Figures 7q and r). ANC for instance, has been between 140 and 158 $\mu Eq\ L^{-1}$ during all years monitored, a range that is much higher than any lakes currently monitored in the Sierra Nevada. Ammonium and nitrate concentrations are low, however, at Patterson, similar to most Sierran lakes.

The relatively high ANC concentrations and the low nitrate concentrations at Patterson suggest little current concern for potential acidification or nutrient issues. A minor increase in pH was identified as statistically significant in 2007.

5.2.7 Mokelumne 14

Mokelumne 14 is a headwater lake at 2545 m elevation near the northwest border of Mokelumne Wilderness about 66 km east-southeast of Placerville and 11 km southwest of Carson Pass. Mokelumne 14 has typically had ANC concentrations between 14 and 20 μEq L^{-1}, undetectable nitrate and sulfate concentrations below 2 μEq L^{-1} (Figure 7s). The south-facing catchment of this 1-ha, 2.5-m deep lake occupies about 45 ha on granodioritic terrain. About two-thirds of the catchment is vegetated and between 2002 and 2004 Secchi disk transparency was to the bottom of the lake. No temporal changes were identified for any chemical constituent for Mokelumne 14 between 2002 and 2007 and the chemistry of this lake approximates that of most other Sierran lakes in the monitoring network (Figure 7).

5.2.8 Lower Cole Creek

Lower Cole Ck Lake is a 6-m deep, 1-ha lake located at 2435 m elevation near the northwest border of Mokelumne Wilderness, about 15 km southwest of Carson Pass. Lower Cole Ck lays in a northwest-facing, 46-ha catchment that maxes out in elevation only about 15 m above lake level. Lower Cole differs from most other lakes in the monitoring network in being the third in a chain of lakes. The two lakes above Lower Cole Ck Lk are equal in area or smaller than Lower Cole Ck. Catchment geology is similar to most of the other Sierra Nevada monitoring lakes, with a preponderance of felsic bedrock. About 80% of the lake catchment is vegetated. Between 2002 and 2004 transparency at Lower Cole Ck was to the bottom (per the Secchi disk procedure).

ANC is relatively high for Lower Cole Ck Lake, compared to other Sierran lakes, and was in the 25 to 33 μEq L^{-1} range between 2002 and 2007. Sulfate and nitrate concentrations have been low at Lower Cole Ck, and suggest no imminent concern for either acidification or nutrients. No statistical trends were identified for Lower Cole Ck Lake and no visual trends in the data are obvious (Figures 7u and v).

5.2.9 Hufford

Hufford Lake occupies a 29-ha, north-facing catchment near the center of Thousand Lakes Wilderness in the southern Cascades. The lake itself occupies about 2.6 ha at 2056 m elevation, below a 2180 m ridge about 69 km west of Redding. Between 2002 and 2004 Secchi disk transparency was 7 m, and the maximum lake depth was about 8 m. This lake also is not a headwater lake and sits 0.2 km below a smaller lake. Volcanic bedrock dominates this Wilderness and because of the small size of the Wilderness the fewer than ten perennial lakes in the Wilderness receive significant recreational use.

During the monitoring period ANC has ranged from 28 to 45 μEq L^{-1}, somewhat higher than for lakes in the central and southern Sierra Nevada (Figure 7m). Similarly, calcium, sodium and magnesium concentrations have been relatively high (Figure 7n). No statistically significant changes in concentrations for any constituents have been identified during the six-year monitoring period.

5.2.10 Caribou 8

At 2131 m elevation, Caribou8 Lake lies in the southern third of Caribou Wilderenss, about 14 km north of Lake Almanor and 48 west northwest of Susanville. The lake is about 1 ha in area within an east-facing catchment of 32 ha area. In 2002 Caribou8 was transparent to the bottom of its 3 m maximum depth. About three-quarters of the terrain in the Wilderness at the elevation of Caribou8 is a blanket of lodgepole pine and red fir.

ANC at Caribou8 has typically been in the mid-20 μEq L^{-1} range (Figure 7k), with no recent single year change meeting the 30% threshold. Compared to other lakes in the R5 monitoring network, Caribou8 has relatively high concentrations of magnesium—atypically higher than calcium concentrations—and relatively low sodium concentrations. These differences may be due to the preponderance of volcanic

terrain in the Wilderness. Since the beginning of monitoring of Caribou8 in 2002, sodium concentrations have declined significantly, at a rate of 0.27 μEq L^{-1} per year. This is the largest rate of change thusfar for any constituent at any lake identified in the monitoring program. Nevertheless, the change is only about 1 μEq L^{-1}, from 8.5 to 7.5. Although this change does not appear to be practically significant, sodium at Caribou8 will be tracked closely in future surveys.

5.3 Elevated Concentrations East of the Sierran Crest

In 2005 lakes east of the Sierran crest in John Muir and Ansel Adams Wildernesses had higher nitrate and sulfate than lakes in Wildernesses west of the crest (except South Warner, which also is located east of the crest of the southern Cascades). The 2007 data further support elevated nitrate and sulfate concentrations in lakes east of the mountain crests. The sample size is smaller in 2007 and no effort is made here to statistically test east-west differences. Mean and median concentrations (μEq L^{-1}) for the 2007 samples are grouped by eastern versus western location below:

	East	West
Nitrate mean	3.27	0.7
Nitrate median	0.78	0.02
Sulfate mean	19.24	2.96
Sulfate median	13.16	2.69

"Eastern lakes" are defined as all of those in South Warner and Hoover Wildernesses and those east of the Sierra crest in John Muir and Ansel Adams, with all other lakes "western lakes".

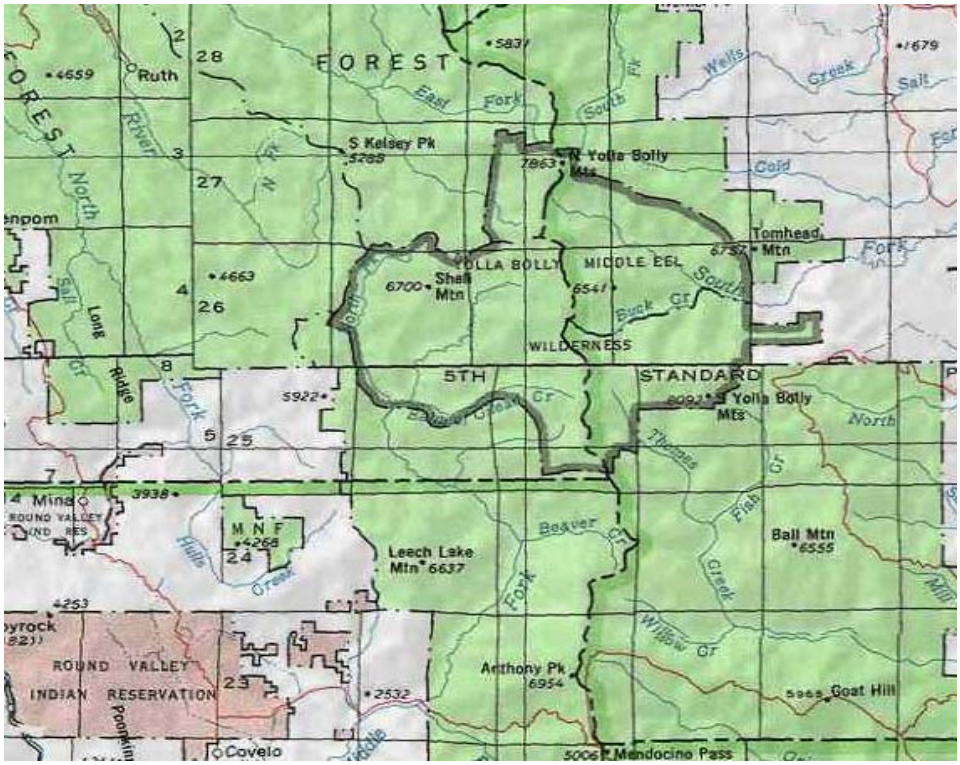
An example of an east side lake with high sulfate and nitrate concentrations is Dana Lake, located at the northern end of Ansel Adams near Yosemite National Park. This lake was one of the first identified in the monitoring program to have elevated sulfate and nitrate concentrations compared to the other lakes sampled. In 2007 Dana again had relatively high nitrate and sulfate concentrations (Figure 8). The Dana Lake concentrations have been consistently greater than either the mean or median of the other lakes each year, and in some years one or two orders of magnitude greater. A variety of factors may be the cause of the high concentrations (Berg 2007), with geologic sources of sulfate a prime candidate and atmospheric deposition from sources in the alkaline Great Basin a nitrate source.

6.0 Yolla Bolly Wilderness Lake Sampling

Yolla Bolly-Middle Eel Class I Area (Figure 9), located in the California north Coast Range (Figure 1) contains approximately one dozen small lakes and ponds. Yolla Bolly's 60,700 ha (150,000 acres) cross the crest of the Coast Range on sedimentary and metamorphic terrain. Yolla Bolly is relatively close to pollution sources in the San Francisco Bay Area and the southern Sacramento Valley. No lakes in Yolla Bolly Wilderness are currently monitored by the Forest Service. To begin an assessment of the potential for a systematic lake monitoring program in Yolla Bolly, two lakes, Long and Square, were sampled in summer 2007. These two lakes were among five surveyed by the FS for pH in the 1980s. No other known lake chemistry is otherwise available for Long or Square Lakes.

Long and Square Lakes are both small headwater lakes located about 1 km apart , of 0.3 and 0.65 ha area respectively. They lie in north-facing catchments at 2,130 m elevation just below the highest peak in Yolla Bolly Wilderness, Mt. Linn. Square Lake has been described as a pond set in a glacial cirque. Besides their chemistry, little information is known about the qualifications of Long and Square lakes for long-term monitoring. They are located less than two miles from a trailhead, implying easy accessibility but potentially high recreational use**.**

Figure 9. Location of Yolla Bolly-Middle Eel Wilderness in the northern Coast Range.


FOREST
Ruth
S Kelsey Pk
5288
N Yolla Bolly
Mts
7863
Tomhead
Mtn
YOLLA BOLLY
MIDDLE EEL
WILDERNESS
Shell
Mtn
6700
6541
5TH
STANDARD
S Yolla Bolly
Mts
8092
Leech Lake
Mtn 6637
Bell Mtn
6555
Anthony Pk
6954
Goat Hill
5965
ROUND VALLEY
INDIAN RESERVATION
Covelo
Mendocino Pass
5000
M N F
4266
Wells
Creek
Salt
Cold
Buck
Thomas
Beaver
Willow
Hull
Creek
Ridge
Long
Ridge
Fork
East
Fork
South
Fork
North
Fork
South
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substantial within-year variability; the ANC value would be some unknown "distance" between the annual maximum and minimum. The annual low best characterizes lake sensitivity to acidification. Consequently the LAKES project targeted early summer sampling. The early summer period trades off the potential for thermal stratification—with the consequent need for both shallow and deep lake sampling in order to completely characterize lake chemistry—with the benefit of a tighter quantification of ANC.

An alternative to early summer sample collection is collection after the turn-over, to simplify procedures and reduce the cost of sample collection, at the risk of obfuscating the quantification of ANC. The ramifications of such a switch need to be comprehensively understood and debated. To begin to assess potential differences in lake chemistry at LAKES project lakes over the summer and early autumn period, samples were collected in 2006 and 2007 two or three times between June and October. This section also assesses differences in chemical concentrations among samples collected (1) at shallow mid-lake locations (epilimnion) compared to shoreline/outlet locations, and (2) deep mid-lake locations (hypolimnion) compared to shoreline/outlet locations.

7.1 Chemical Differences Between Early Summer and Late Summer

In an effort to better understand potential seasonal changes in lake chemistry and to further refine the scheduling of lake water sample collection, multiple sample collections were made at selected lakes in 2006 and 2007. Four lakes (Powell (Emigrant Wilderness), Treasure (John Muir Wilderness), Cascade (Hoover Wilderness) and Moat (Hoover Wilderness)) were sampled from their shorelines in mid or late June 2007 and again in October 2007. In 2006 two lakes (Powell and Long) were sampled at their outlets, epilimnion or hypolimnion two or three times between July and October.

June-to-October changes in 2006 and 2007 generally paralleled the UC Santa Barbara results (Figure 10), at least in terms of the direction of change. Magnitude of change varied however, and this variability, in combination with the small sample size, allows only preliminary, graphical information to be presented; no statistical assessment is undertaken. More within-year sampling, ideally at the traditional end-of-snowmelt period and late September or early October when the lakes should be thermally mixed, is needed to better quantify within-year concentration differences and to better understand options for changing the timing of sample collections.

7.2 Chemical Differences Between Outlet and Mid-lake Sampling Locations

Sample collection could be hastened and simplified if samples were collected along the lake shoreline, rather than from mid-lake locations. Mid-lake sampling, however, provides valuable information that cannot be collected from shore. The sampling protocol currently includes mid-lake sampling, but the potential for significant resource savings from shoreline/outlet sampling cannot be ignored. To investigate the potential to shift to solely shoreline/outlet sampling in 2007 nine pairs of epilimnion and outlet samples were collected at long-term monitoring lakes. Fourteen similar pairs were collected in earlier years. For this 23-sample dataset significant differences were not identified (at the 0.05 level) for ANC, nitrate, sulfate or calcium using the Wilcoxon paired sign test. This implies that there were no statistically significant differences in concentrations for the four constituents between epilimnion and outlet samples (at α=0.05).

In five paired outlet and hypolimnion samples from 2006 and four paired outlet and hypolimnion samples from 2007, ANC and calcium differed significantly but sulfate and nitrate did not. The total of nine samples is still very small for statistical comparison, so results are preliminary and it is premature to speculate on causes for these results. Nevertheless, based on this result, the ANC and calcium concentrations do differ between the hypolimnion and outlet samples, suggesting that outlet-only sampling will not document the ANC and calcium chemistry of the deeper waters.

8.0 Diatom Sampling

As part of an effort to determine "critical loads" for nitrogen in selected Wilderness Areas in the Sierra Nevada, "short core" diatom samples from lake sediments were collected at six lakes under Forest Service jurisdiction in the Sierra Nevada in 2007 (Sickman et al. 2006). One of these lakes, Moat in Hoover Wilderness, is being sampled as well for water chemistry and transparency. The diatom project is a partnership with Professor James Sickman (University of California Riverside) and the National Park Service. The short core samples will be related to long core samples that will allow reconstruction of limnetic nitrogen values over a period of approximately the last 100-200 years. Funding permitting, between October 2008 and April 2010, the following tasks will be completed—

- chemical analysis of sediments in the long cores
- enumeration of diatoms from the long cores
- development of a trophic state model
- identification of trends in diatom species in the long cores
- deposition modeling
- reports and a draft manuscript from the study.

9.0 Topics from Previous Years

Three aspects of the monitoring program that have been previously discussed are (1) the option to sample at lake outlets or along the shoreline, (2) concerns with the ongoing ion imbalance and (3) analysis of the zooplankton samples. Progress on the option for outlet sampling is discussed above. To address the ion imbalance, samples collected in 2007 are being tested for dissolved organic carbon. However, results of the testing were not available at the time of writing of this report. When the results become available they will be integrated into this report, or added as an addendum.

The 2004 recommendation on zooplankton remains current: analyze the collected zooplankton data and assess pros and cons of resumed zooplankton. This recommendation links into any future decision to suspend mid-lake sample collection. Although zooplankton can be collected from the shoreline a different procedure would be used, potentially requiring a "calibration" period wherein both mid-lake and shoreline zooplankton collection was conducted to assure continuity of the data record.

10.0 Conclusions

Completion of the network of long-term monitoring lakes in 2007 will reduce the expense of monitoring and extend the ability to identify temporal and spatial trends in lake chemistry changes at twelve Wildernesses—and 25 lakes--in the Sierra Nevada and northeastern California.

The overall quality of the 2007 laboratory analysis improved with respect to several prior years. Application of commonly-used quality assurance techniques identified no issues other than continuation of a long-standing imbalance between cations and anions and overly long transit time for some samples. Recommendations to address these issues are given at the beginning of this report.

Ten lakes were assessed for temporal trends in their acid-base chemistry. Although statistically significant changes in lake chemistry were identified at five lakes, the changes were generally small and not associated with acidification or nutrient buildup. Statistically significant sulfate decreases at the two lakes with the longest records may reflect documented reductions in sulfur deposition in many locations in the United States. These trend results are preliminary for most of the lakes and could change as more data are collected.

Lakes in Wildernesses located to the west of the crest of the Sierra Nevada generally have similar chemistries. Wildernesses located east of the crest, including South Warner and Hoover Wildernesses and parts of Ansel Adams and John Muir, are more directly exposed to atmospheric deposition originating in the drier, more alkaline Great Basin terrain. Nitrate and sulfate concentrations at these lakes are higher and more variable than at Wildernesses located exclusively on western slope of the Sierra Nevada.

To better understand "critical loads" of nitrogen from atmospheric deposition to high elevation lakes, several lake bottoms were cored in 2007 to reconstruct nitrogen values over the last 100-200 years. To redeem the potential of the 2007 effort, additional coring and diatom assessment will be needed in 2008 and possibly 2009.

There is a potential to revise the monitoring protocol to sample only from lake outlets in early autumn. This is premature at this time and additional paired outlet and mid-lake samples should be collected in during both the traditional early summer sampling period and in early autumn to help address this alternative. Also the zooplankton data collected to date should be analyzed before a decision is made to abandon mid-lake sampling.

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